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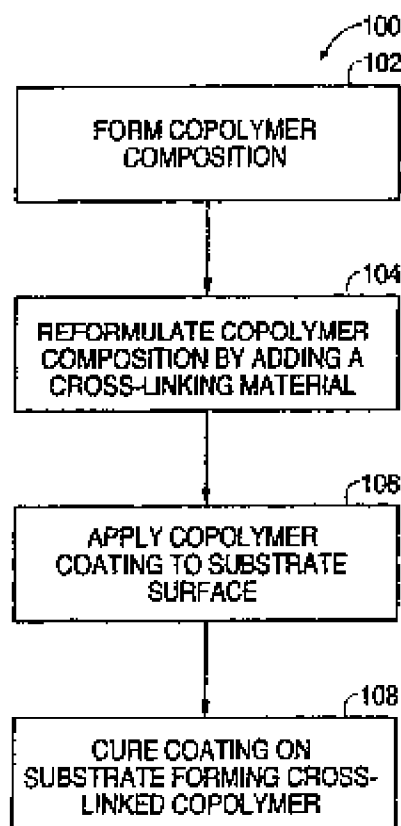
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(54) Title: **ANTI-CORROSION COATING AND TAPE FOR ELECTRONIC CABLE**



(57) Abstract: A method for forming an anti-corrosion coating on a substrate surface includes reformulating a copolymer composition with a cross-linking material. The resulting cross-linked copolymer composition is then applied to the substrate surface and cured. The cross-linked copolymer composition can include an acrylic-acid based copolymer and a carboxyl based catalyst. The substrate can include foils, multi-ply laminates of aluminum, and plastic film. The anti-corrosion coating is to be applied to metals and films that are used in shielding for electronic cables and enhances their functionality by providing electrical, moisture, and/or thermal shielding, while providing a bonding layer to some olefinic compounds, advantageous in some shielded cable applications.

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ANTI-CORROSION COATING AND TAPE FOR ELECTRONIC CABLE

BACKGROUND OF THE INVENTION

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Field of the Invention

The present application claims benefit of priority of U.S. Provisional Application No. 60/160,988 filed on October 22, 1999.

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The present invention is directed to a method for forming an anti-corrosion coating on metal foils, multi-ply laminates of metal, in particular aluminum, and plastic film, and plastic film used for electronic cables.

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Conventional electronic cables, such as coaxial and twisted pair cables, use metal tapes or foils to reduce the interference of near- and far-field EMI/RFI on the signal being delivered and to reduce the emission of electrical signals from the cable. However, over time, a buildup of metal oxides on the foil surface (due to corrosion) will, eventually, render the cable useless for this purpose by reducing the effectiveness of the transmitted signal.

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One conventional method of reducing the negative effects of corrosion is to use flooding compounds, such as wax and/or oil based materials that are spread on the cable. Upon cooling of the cable, the physical properties of the flooding compounds change, leaving a waxy residue on the cable that must be removed prior to use. Thus, this method is undesirable in many applications because of the

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expense, the degradation at elevated temperatures, and the environmental effects of the flooding compounds.

What is needed is a metal tape or foil that can be used for the fabrication of electronic cables that will not be subject to the corrosion effects currently seen on conventional tapes and that also facilitates straightforward manufacturing capabilities.

SUMMARY OF THE INVENTION

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In view of the foregoing, it would be desirable to provide a process for the fabrication of a tape that eliminates the effects of corrosion when used as a shield in electronic cable. According to one embodiment of the present invention, a method for forming an anti-corrosive coating on a substrate surface includes reformulating an copolymer composition with a cross-linking material. The resulting copolymer composition is then applied to substrate surface and cured to form a cross-linked copolymer. According to an embodiment of the present invention, the substrate can include metal foils, multi-ply laminates of metal and plastic films, and plastic film.

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In another embodiment, the substrate is a metal foil having a thickness of about 0.00025 inches to about 0.004 inches. In yet another embodiment of the present invention, the resulting surface coating can provide anti-corrosion properties to the metal and offer a bonding layer to olefinic compounds, advantageous in some shielded cable applications.

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Further features and advantages of the invention, as well as the structure and operation of various embodiments of the invention, are described in detail below with reference to the accompanying drawings.

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BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated herein and form part of the specification, illustrate, but do not limit, the present invention and, together with the description, further serve to explain the principles of the invention and to
10 enable a person skilled in the pertinent art to make and use the invention.

Figure 1 is a flowchart of a process of forming an anti-corrosive coating according to an embodiment of the present invention.

Figure 2 is a schematic diagram of an electronic cable that incorporates
15 metal layers coated with an anti-corrosion coating.

DETAILED DESCRIPTION OF THE INVENTION

The present invention pertains to a method for the fabrication an anti-
20 corrosion tape to be used in electronic cables. Further, the present invention pertains to an anti-corrosion coating that includes a cross-linked copolymer composition that is applied to metal foils or multi-ply laminates of metal and plastic film, and plastic film found within an electronic cable. Preferably, the metal foil has a thickness from 0.00025 inches to about 0.004 inches. The present invention

provides a new tape design that substantially reduces the effect of corrosion when used as a shield in electronic cables. In addition, the present invention provides a new anti-corrosion tape design while forming a bonded tape that is useful in some shielded cable applications. The new tape design utilizes a solvent-based coating that can be applied as a very thin layer on the metal surface. Preferably, the solvent is water.

Fig. 1 shows a flowchart of the process 100 of forming an anti-corrosive coating according to one embodiment of the present invention. The anti-corrosive coating comprises a cross-linked copolymer coating that is designed to optimize the life of metals to which it is applied.

In step 102, a copolymer composition is formed. This composition can be in the form of a mixture or in solution. Preferably, the composition is formed through dispersion in an aqueous (or other solvent-based) solution. According to the invention, the constituents of the composition include from about 10% to about 40% copolymer (solid) and about 60% to about 90% water (or other solvent) solution, based on the combined weight of the polymer and solvent. According to one embodiment, the constituents of the composition include about 25 wt. % copolymer (solid) and about 75 wt. % water (or other solvent) solution, based on the entire weight of the polymer and solvent.

In a preferred embodiment, the copolymer is an acrylic acid-based copolymer, such as ethylene-acrylic acid, ethyl-methyl-acrylic acid, ionomers, and the like. For example, the copolymer can include about 5 wt. % to about 30 wt. %

acrylic acid and 70 wt. % to 95 wt. % ethylene, based on the weight of the copolymer. Alternatively, the acrylic acid-based copolymer can comprise an ethyl-methyl-acrylic acid copolymer, having a concentration of about 13%, based on weight of the copolymer. Many acrylic acid-based copolymers, such as an
5 ethylene-acrylic acid copolymer consisting of about 20 wt. % acrylic acid, based on the weight of the copolymer, can be purchased from commercial vendors.

In step 104, the copolymer composition is reformulated. The reformulation step includes adding a cross-linking material, such as a catalyst, to the copolymer
10 composition. These constituents can be mixed according to conventional techniques.

The cross-linking material improves the bonding of the composition to metal. In a preferred embodiment, the catalyst comprises aziridine, or other
15 carboxyl reactive crosslinking agents, such as urea-formaldehyde, epoxies, and the like, which can be commercially purchased. The amount of catalyst can be from about 1 wt. % to about 10 wt. %, based on the weight of the coating solution. Further, the reformulation step can also include adding an amount of solvent to further decrease the concentration of solids in the composition. This reformulation
20 can be performed at any temperature above the freezing point, such as room temperature. This reformulation provides bondability of the coating to other materials to ensure end product functionality, namely anti-corrosive properties in cable applications.

In step 106, the resulting copolymer composition is applied to a surface of a substrate as a coating. The substrate can be a metal foil, a multi-ply laminate of metal and plastic film, or plastic film. Preferably, the metal can be aluminum, copper, steel, or other metals, that can be used in electronic cabling. For example, the substrate can comprise thin layers of aluminum, on the order of .00035 inches in thickness, that are bonded on one or both sides of a plastic film.

The coating step can be performed by any number of conventional techniques, including, but not limited to gravure coating, roll coating, and spray-coating. According to the invention, the applied coating can be a very thin layer, with coating thicknesses ranging from about 0.00005 inches to about 0.001 inches.

Preferably, this coating is to be applied to foils, such as metal foils from 0.00025 inch to about 0.004 inch in thickness, or multi-ply laminates of metal, such as aluminum, and plastic film that are used in shielding (or other barrier) for electronic cables and enhances their functionality by providing a corrosion-resistant electrical, moisture, and/or thermal shielding. The resulting coating is also resistant to most conventional solvents. In addition, the coating can be applied to one or more metal surfaces of multiple laminated substrates, i.e., thin layers of metal (e.g., Al or Cu) laminated to plastic based films. Such multiple laminated substrates can be commercially purchased under the trade name LAMIGLAS. The coating can also be applied to thin layers of metal laminated to thin layers of plastic film and/or woven or non-woven fabrics, such as those sold under the trade name INSULFAB.

After the copolymer coating is applied to the surface of the substrate, the coating is cured on the substrate surface in step 108. In the curing step, the solvent is dried off and the catalyst is activated to begin cross-linking. For example, curing can be accomplished by placing a coated metal material in an oven heated at 150° to 200° for several seconds. Alternatively, the coating may also be cured at lower temperatures for longer periods of time, or in an oven at elevated temperatures for a shorter period of time, as would be apparent to one of skill in the art given the present description. Other methods of drying/curing include EB, UV, IR, and other conventional techniques. Further, the resulting coating is transparent and does not mask the application onto existing products. Colored coatings can be obtained by adding pigments to the composition.

According to the present invention, a cross-linked copolymer coating will not seal when the exposed surface of the coating is placed in contact with another metal. In other words, by adding the cross-linking material to the ethylene-acrylic acid copolymer, the resulting composition becomes a thermoset. The addition of the cross-linking material/catalyst increases the adhesion of the coating to the metal substrate. Once the coating is cured on the surface of the metal, the exposed surface of the coating will not bond to another metal surface. These characteristics make this anti-corrosive coating particularly useful for the industrial fabrication of metal rolls, which are used in the mass production of electronic cable. For example, the metal tape of a large scale fabrication roll can be 66 inches wide and weigh in excess of 4000 pounds. If the coating seals when rolled (i.e., the coating bonds with the back surface of the overlaying metal tape), the tape cannot be later unspooled.

Further, the coating will adhere to some olefinic compounds, such as acrylic acid copolymers, providing a bonded tape, advantageous in some shielded cable applications.

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The coating of the present invention can be applied to one or more metal surfaces in a conventional electronic cable to provide a cable with high resistance to corrosion effects. For example, a coaxial cable 200 is shown in Fig. 2. Cable 200 includes an aluminum braid wire 202, an aluminum foil (either bonded or
10 unbonded) layer 204, and a cable core 206. The cross-linked copolymer coating can be applied to one or more surfaces of foil layer 204. The resulting electronic cable is resistant to corrosion.

Alternatively, the coating of the present invention can also be used in non-
15 insulative applications for any metal product that needs protection from the corrosive effects of moisture.

Examples

An example anti-corrosion coating was formed. The coating was mixed
20 comprising a dispersion of 66 wt. % ethylene-acrylic acid copolymer, 32 wt. % water, 0.1 wt. % defoamer, and 2 wt. % aziridine. This coating was then applied to a LAMIGLAS substrate using a conventional coating technique.

In addition, test samples with a similar coating composition were formed and
25 exposed to a salt water mist for several days. No corrosive effects were found in

the test samples coated with the cross-linked copolymer coating. Samples of aluminum tape coated with the anti-corrosion coating were immersed in 10% salt solution in water at 120 degrees Fahrenheit for several days along with same material in tap water. No corrosion was detected on visual examination of the anti-

5 corrosion coated tape.

Further, large scale coating tests were performed using a coating having a composition similar to the composition described above. In this test, the water-based anti-corrosive coating was applied to an uncoated metal tape roll, having a

10 tape thickness of 0.003 inches, using a conventional technique. The coating thickness was less than 0.0001 inches, on the order of about 0.00005 inches, based on the fact that the coating was uniformly applied at a rate of 0.04 ounces per square yard. After curing, the resulting coating could not be removed by application of several conventional solvents.

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While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope of the invention. Thus, the breadth and scope of the present

20 invention should not be limited by any of the above-described exemplary embodiments.

WHAT IS CLAIMED IS:

1. A method for forming an anti-corrosive coating on a substrate surface, comprising:
 - reformulating a copolymer composition with a cross-linking material;
 - applying said copolymer composition to the substrate surface; and
 - curing said copolymer composition on the substrate surface to form a cross-linked copolymer.
2. The method of claim 1, wherein said copolymer composition is a solvent-based dispersion of about 10% to about 40% solid, based on the weight of the composition, and wherein said copolymer composition is an acrylic acid-based copolymer comprising acrylic acid at a concentration of about 5% to about 30%, based on the weight of the copolymer.
3. The method of claim 2, wherein said acrylic acid-based copolymer comprises acrylic acid at a concentration of about 20% and ethylene at a concentration of about 80 %, based on the weight of the copolymer.
4. The method of claim 1, wherein said reformulating comprises introducing a reactive cross-linking agent to said copolymer composition.
5. The method of claim 4, wherein said reactive cross-linking agent is a carboxyl-based catalyst.

6. The method of claim 4, wherein said reactive cross-linking agent is aziridine at a concentration of about 2 % to about 5 %.
7. A metal tape formed by the process of claim 1.
8. A bonded tape formed by the process of claim 1, wherein the cross-linked copolymer is bonded to an olefinic compound.
9. A metal tape, comprising:
 - a metal substrate, wherein said metal substrate is selected from the group consisting of metal foils and multi-ply laminates of metal and plastic films; and
 - a coating applied to at least one surface of said metal substrate, said coating comprising a copolymer composition that cross-links upon curing.
10. The metal tape of claim 9, wherein said coating comprises a composition of an acrylic acid-based copolymer in a solvent-based dispersion and a carboxyl-based catalyst.
11. The metal tape of claim 10, wherein said coating comprises an aqueous dispersion of about 25 wt. % acrylic acid-based copolymer based on the weight of the coating solution, and wherein said acrylic acid-based copolymer comprises acrylic acid at a concentration of about 5% to about 30%, based on the weight of the copolymer.

12. The metal tape of claim 11, wherein said acrylic acid copolymer comprises acrylic acid at a concentration of about 20% and ethylene at a concentration of about 80 %, based on the weight of the copolymer.
13. The metal tape of claim 11, wherein said coating comprises an aziridine catalyst at a concentration of about 2 % to about 5%, based on the weight of the aqueous dispersion.
14. The metal tape of claim 9, wherein the coating has a thickness of from about 0.00005 inches to about 0.001 inches.
15. The metal tape of claim 9, wherein said metal foil has a thickness of about 0.00025 inch to about 0.004 inch.
16. The metal tape of claim 9, further comprising an olefinic compound bonded to the coating.
17. The metal tape of claim 16, wherein the olefinic compound is an acrylic acid copolymer.
18. An electronic cable, comprising:
a shielding layer coated with a cross-linked copolymer composition.

19. The electronic cable of claim 18, wherein said cross-linked copolymer composition includes an acrylic acid-based copolymer and a carboxyl-based catalyst.
20. The electronic cable of claim 19, wherein said cross-linked copolymer composition comprises an aziridine catalyst at a concentration of about 2 % to about 5%, based on the weight of a solvent-based dispersion containing the copolymer.
21. The electronic cable of claim 18, wherein said shielding layer is selected from the group consisting of metal foils and multi-ply laminates of metal and plastic films.
22. The electronic cable of claim 18, wherein said shielding layer is a metal layer, said metal selected from the group consisting of aluminum, copper, and steel.
23. The electronic cable of claim 18, wherein said shielding layer comprises multi-ply laminates of aluminum, and wherein said cross-linked copolymer composition is a coating on one or more surfaces of said shielding layer, said coating having a thickness of from about 0.00005 inches to about 0.001 inches.
24. The electronic cable of claim 18, wherein said metal foil has a thickness of about 0.00025 inch to about 0.004 inch.
25. The electronic cable of claim 18, wherein the cross-linked copolymer composition is bonded to an olefinic compound.

26. The electronic cable of claim 25, wherein the olefinic compound is an acrylic acid copolymer.

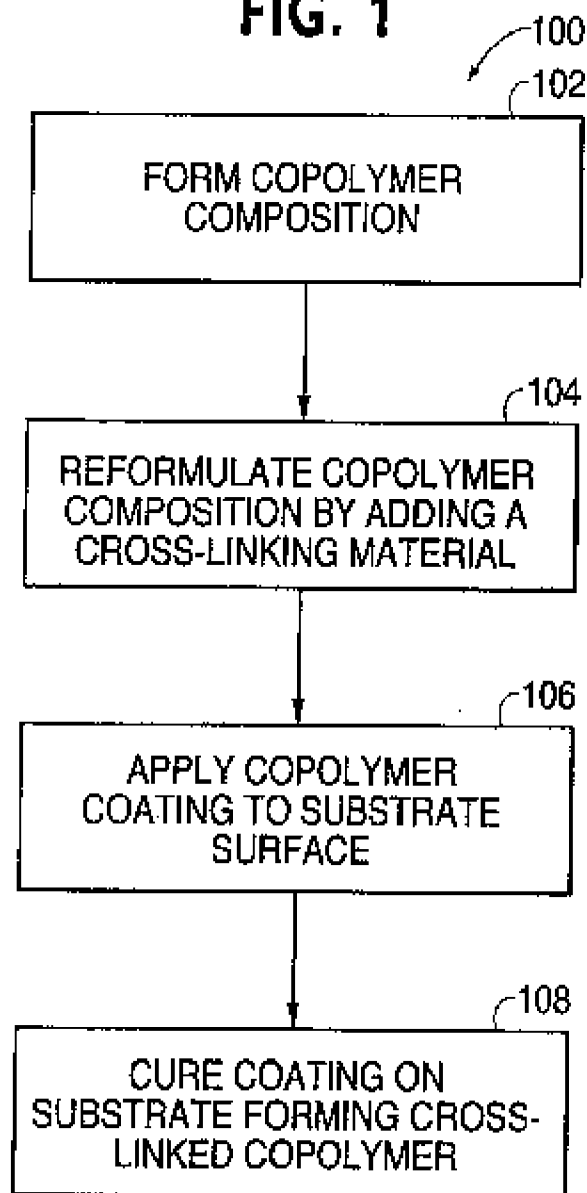
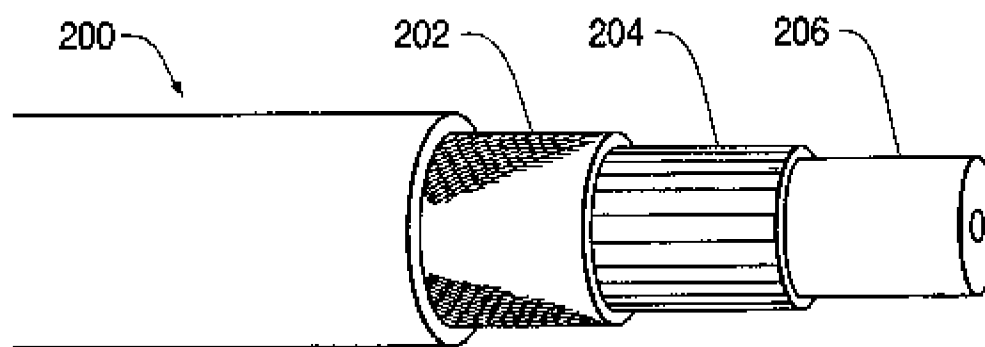
FIG. 1

FIG. 2

INTERNATIONAL SEARCH REPORT

Internal . Application No
PCT/US 00/29007

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B05D7/00 H01B3/44 C09D123/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B05D H01B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 10023 A (BASF AG ; BRODT GREGOR (DE); KINGMA AREND JOUKE (DE); SCHROEDER ULR) 12 March 1998 (1998-03-12) abstract; claims 1-14	1-5
Y	page 4, line 39 -page 5, line 43 page 10, line 25-35	1-26
Y	US 3 908 066 A (PARKINSON ROBERT E) 23 September 1975 (1975-09-23) abstract; claims 1-15 column 4, line 30-55	1-26
A	US 4 273 695 A (GREENE ROBIN N ET AL) 16 June 1981 (1981-06-16) abstract; claims 1-14 column 1, line 27-31 column 2, line 5-8, 23, 49-56 column 3, line 10-16, 22, 23	1-26
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/29007

D.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 198628 Derwent Publications Ltd., London, GB; Class A81, AN 1986-179937 XP002158892 & JP 61 113676 A (NIPPON STEEL CORP), 31 May 1986 (1986-05-31) abstract</p>	7-17
A	<p>US 3 829 340 A (DEMBIAK M ET AL) 13 August 1974 (1974-08-13) abstract; claims 1-10 column 2, line 37 -column 4, line 51</p>	18-26
A	<p>US 3 730 792 A (FROST C ET AL) 1 May 1973 (1973-05-01) abstract; claim 1</p>	1-26

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internet: JI Application No

PCT/US 00/29007

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9810023 A	12-03-1998	DE 19636077 A EP 0923623 A US 6146704 A	12-03-1998 23-06-1999 14-11-2000
US 3908066 A	23-09-1975	BE 818229 A LU 70609 A NL 7410845 A US 3839256 A CA 1024284 A DE 2422367 A FR 2228827 A GB 1422920 A JP 50048037 A ES 426122 A IT 1014164 B RO 71326 A SU 772486 A	29-01-1975 28-11-1974 17-02-1976 01-10-1974 10-01-1978 21-11-1974 06-12-1974 28-01-1976 28-04-1975 01-11-1976 20-04-1977 15-04-1980 15-10-1980
US 4273695 A	16-06-1981	AU 540066 B AU 6639181 A CA 1174786 A EP 0056509 A JP 1011674 B JP 1527614 C JP 57139149 A	01-11-1984 29-07-1982 18-09-1984 28-07-1982 27-02-1989 30-10-1989 27-08-1982
JP 61113676 A	31-05-1986	NONE	
US 3829340 A	13-08-1974	CA 932414 A US 3819434 A US 3823747 A US 3703605 A	21-08-1973 25-06-1974 16-07-1974 21-11-1972
US 3730792 A	01-05-1973	NONE	

